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X-Ray Diffraction Powder Studies of Some Dithiol Diesters of Long Chain Acids

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D. A. Lutz and **L. P. Witnauer**, Eastern Regional Research Laboratory[1] Philadelphia, Pennsylvania; **George S. Sasin** and **Richard Sasin**, Drexel Institute of Technology, Philadelphia, Pennsylvania

ABSTRACT

X-ray diffraction powder data are reported for 25 mono- and dithiol diesters of straight chain aliphatic acids where the acid portion of the molecule consists of one of the following acids: octanoic, decanoic, dodecanoic, tetradecanoic, hexadecanoic or octadecanoic acids, and where the thiol portion consists of one of the following: 2-mercaptoethane, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol or 1,5-pentanedithiol. The individual compounds can be identified and distinguished by the long spacing data. The compounds crystallize in tilted monomolecular layers.

INTRODUCTION

A RECENT PUBLICATION (1) describes the synthesis of monothiol and dithiol diesters of long chain acids. Many of these compounds are solid crystalline materials whose melting points are above room temperature. These compounds are suitable for a study by X-ray diffraction. This paper reports X-ray studies of 25 mono- and dithiol diesters of straight chain aliphatic acids containing an even number of carbon atoms, namely, octanoic, decanoic, dodecanoic, tetradecanoic, hexadecanoic, and octadecanoic acids. The general formula of the mono diesters is $R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}(CH_2)\text{-}S\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$ and of the dithiol diesters is $R\text{-}\overset{O}{\overset{\|}{C}}S\text{-}(CH_2)_n\text{-}S\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$ where n varies between two to five.

EXPERIMENTAL

The synthesis and the purification of the compounds used in this study were described elsewhere (1). Most of these compounds were crystallized from acetone, hexane and chloroform at room temperature. X-ray diffraction measurements were made with a General Electric XRD-3 direct recording unit, using nickel-filtered CuKα radiation (λ = 1.5405 Å), 1° beam slit, 0.1° detector slit, medium resolution soller slit, scanning speed 2° /min, chart speed 60 in./hr. The X-ray data listed in Table I were obtained from unground samples. Thin layers measuring approximately 0.5 in. by 1.0 in. were firmly pressed on a glass slide to insure adherence. The long spacings listed in Table I are the average of several orders taken from oriented samples. The first few orders were often not included because of the limited accuracy with which they could be measured. Complete X-ray powder data were obtained from ground (unoriented) samples but are not included in this paper due to the large amount of space that would be required to describe them. Shown in Figure 1 are the long spacings of the compounds studied plotted against the number of carbon atoms in each of the individual acid portions of the molecule.

RESULTS AND DISCUSSION

All compounds investigated can be identified and distinguished on the basis of the X-ray diffraction long spacing data. The compounds investigated gave X-ray diffraction patterns which contained a large number of relatively sharp diffraction peaks. This is characteristic of the highly crystalline nature of these compounds. The same crystalline forms appeared irrespective of the solvent used, namely, hexane, acetone, or chloroform. Three compounds, namely, 1,2-ethanedithiol didodecanoate, 1,4-butanedithiol didecanoate and 1,4-buthanedithiol didodecanoate, always crystallized in two polymorphic forms. The number of orders used in the calculation of each long spacing is given in Table I.

A plot of the total number of carbon atoms in each acid chain (y) against the long spacings (x) of the 2-mercaptoethanol diesters (Fig. 1) showed that the long spacing values fall in a straight line whose equation as determined by the method of least squares is $y = 0.444143x - 2.82$. This would indicate that the 2-mercaptoethanol diesters studied crystallize in the same polymorphic form. A plot of the total number of carbon atoms in each acid chain (y) against the long spacings (x) of the 1,2 ethanedithiol diesters (Fig. 1) showed that the long spacing values fell on two straight lines. The values of the dioctanoate, didecanoate, and the smaller long spacing

[1] E. Util. Res. Dev. Div., ARS, USDA.

TABLE I

Long Spacings of Mono- and Dithiol Diesters

Compound	Total atoms in chain[a]	Long Spacing Å	No. of orders used	Crystallized form
2-Mercaptoethanol didecanoate	24	28.85 ± .0279	8	A
2-Mercaptoethanol didodecanoate	28	33.34 ± .0114	14	CHA
2-Mercaptoethanol ditetradecanoate	32	37.88 ± .0179	10	CHA
2-Mercaptoethanol dihexadecanoate	36	42.40 ± .0184	15	CHA
2-Mercaptoethanol dioctadecanoate	40	46.84 ± .1023	6	CHA
1,2-Ethanedithiol dioctanoate	20	23.70 ± .0203	6	CHA
1,2-Ethanedithiol didecanoate	24	28.46 ± .0206	8	CHA
1,2-Ethanedithiol didodecanoate	28	33.04 ± .0199	8	CHA
		33.92 ± .0183	10	
1,2-Ethanedithiol ditetradecanoate	32	38.40 ± .0099	15	CHA
1,2-Ethanedithiol dihexadecanoate	36	42.92 ± .0179	14	CHA
1,2-Ethanedithiol dioctadecanoate	40	47.40 ± .0420	12	CHA
1,3-Propanedithiol didecanoate	25	28.12 ± .0350	7	CHA
1,3-Propanedithiol didodecanoate	29	32.28 ± .0106	14	CHA
1,3-Propanedithiol ditetradecanoate	33	36.47 ± .0108	18	A
1,3-Propanedithiol dihexadecanoate	37	40.72 ± .0159	15	CHA
1,4-Butanedithiol dioctanoate	22	26.28 ± .0115	9	CHA
1,4-Butanedithiol didecanoate	26	30.78 ± .0297	5	CHA
		31.48 ± .0878	3	
1,4-Butanedithiol didodecanoate	30	35.24 ± .0316	5	CHA
		35.96 ± .0153	17	
1,4-Butanedithiol ditetradecanoate	34	40.52 ± .0105	11	CHA
1,4-Butanedithiol dihexadecanoate	38	45.03 ± .0124	18	CHA
1,5-Pentanedithiol didecanoate	27	25.61 ± .0986	4	CHA
1,5-Pentanedithiol didodecanoate	31	29.14 ± .0127	10	CHA
1,5-Pentanedithiol ditetradecanoate	35	32.74 ± .0165	10	CHA
1,5-Pentanedithiol dihexadecanoate	39	36.26 ± .0328	11	CHA
1,5-Pentanedithiol dioctadecanoate	43	39.76 ± .0397	5	CHA

[a] Hydrogen and carbonyl oxygen atoms not included.
H = *n* Hexane. A = Acetone. C = Chloroform.

value of one polymorphic form of the didodecanoate fell on a line whose equation as determined by the method of least squares is y = 0.428212x − 2.1612, whereas the larger long spacing value of the other polymorphic form of the didodecanoate and the values of the ditetradecanoate, dihexadecanoate, and the dioctadecanoate fell on a line whose equation as determined by the method of least squares is y = 0.444838x − 3.0871. The data indicate that a change in molecular packing (2) takes place when the number of carbon atoms in the acid chain is greater than 12 for this series.

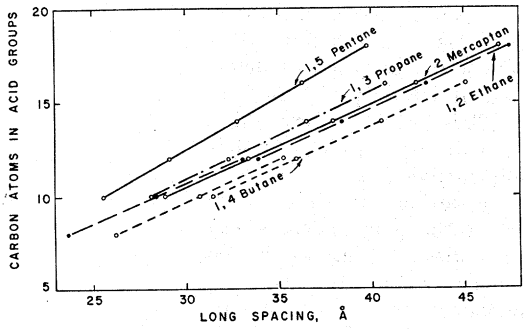

Fig. 1

The relative amounts of the two polymorphic forms found in the X-ray spectra of 1,2-ethanedithiol didodecanoate appeared to be a function of the solvent's polarity. The higher the polarity of the solvent the higher the relative amount of the polymorphic form exhibiting the larger value of the long spacing was present in the spectra.

When the total number of carbon atoms in each acid chain (y) was plotted against the long spacing values (x) of the 1,3-propanedithiol diesters (Fig. 1), their values fell on a straight line whose equation as determined by the method of least squares is y = 0.476292x − 3.3844. Only one polymorphic form was observed. A similar plot of the long spacings of the 1,4-butanedithiol diesters (Fig. 1) showed that the long spacings values fell on two straight lines. The long spacing values of the dioctanoate and the smaller long spacing values of the didecanoate and the didodecanoate, both of which showed the presence of two polymorphic forms fell on a line whose least squares equation is y = 0.446425x − 3.7365, whereas the larger long spacing values of the other polymorphic forms of the didecanoate and the didodecanoate and those of the ditetradecanoate and the dihexadecanoate fell on a

TABLE II

Least Squares Equations for Mono- and Dithiol Diesters
Y (carbon atoms in each side chain) = B x (long spacing) + A

Series	B	A
2-Mercaptoethanol diesters	0.444143	−2.82
1,2-Ethanedithiol diesters (low members)	0.428212	−2.1612
1,2-Ethanedithiol diesters (high members)	0.444838	−3.0871
1,3-Propanedithiol diesters	0.476292	−3.3844
1,4-Butanedithiol diesters (low members)	0.446425	−3.7365
1,4-Butanedithiol diesters (high members)	0.442375	−3.9208
1,5-Pentanedithiol diesters	0.564639	−4.4637

straight line whose least squares is y = 0.442375x − 3.9208. A change in molecular packing (2) is indicated when the acid chain contains 10 to 12 carbon atoms in this series. A similar plot of the 1,5 pentanedithiol diesters (Fig. 1), gave a straight line whose least squares equation is y = 0.564639x − 4.4637. Only one polymorphic form was observed in this series. The above results are summarized in Table II.

Given in Table III are the results of the least squares analysis for each series studied where the y parameter was taken as the total number of atoms in the chain (Table I). The limits about B, the linear regression coefficient, and A, the y intercept given in Table III are the 95% confidence limits. Also given in Table III are the reciprocals of the linear regression coefficients in units of angstrom units per additional carbon atom. The average increments in long spacings per additional carbon atom were all less than the maximum calculated increment for a carbon atom, 1.306 Å; therefore, these compounds crystallize in tilted mono- molecular layers.

Examination of Table III shows that significant overlap exists in the 95% confidence ranges in both the B and A parameters of the low members of 1,2-ethanedithiol diester and the lower members of the 1,4-butanedithiol diester series. Therefore the packing in the solid state of these two series is probably isomorphic. Examination of Table III shows that significant overlap exists in the 95% confidence ranges in both the B and A parameters of the high members of 1,2-ethanedithiol diester and the high members of the 1,4-butanedithiol diester series. Therefore the packing of these two series is also probably isomorphic.

Examination of Table III shows that the linear regression coefficient B for the 2-mercaptoethanol diester series is almost identical to those of the high members of both the 1,2-ethane and the 1,4-butanedithiol diester series. A study of the 95% confidence limits also shows considerable overlap. In contrast the y intercepts A of the three series shows only insignificant overlap. However, the covalent radius for sulfur is 1.04 Å, whereas the covalent radius for oxygen is only 0.74 Å (3). The difference in their covalent diameter is therefore 0.60 Å. If one assumes that this difference is equal to the difference in the longest crystallographic axis that one would expect between the same dithiol and monothiol derivative and dividing by 1.306 Å to obtain for the difference in the A parameter one gets a figure of 0.46 Å. If one subtracts this value of 0.46 Å algebraically from the A parameter of the 2-mercaptoethanol diester series and assumes that the 95% confidence limits are relatively unchanged, one now gets considerable overlap in the 95% confidence ranges of the A parameters of these three series. This would lead one to suspect that these three series crystallize isomorphically. This, however, cannot be said with certainty without further study.

Normally an alternation in long spacing between members in a homologous series containing even and odd numbers of carbon atoms is characteristic of long chain compounds (4). Examination of Table III shows that the curves resulting from the 1,3-propanedithiol

TABLE III

Least Squares Equation and 95% Confidence Limits for Mono- and Dithiol Diesters
y (total atoms in chain) = B × (long spacing) + A

Series	B	A	$\frac{1}{B}$ (Å per additional carbon atom)
2-Mercaptoethanol diesters	0.888287 ± 0.004775	−1.6310 ± 0.183242	1.126
1,2-Ethanedithiol diesters (low members)	0.856425 ± 0.041177	−0.3225 ± 1.1807	1.168
1,2-Ethanedithiol diesters (high members)	0.889676 ± 0.003883	−2.1742 ± 0.1588	1.124
1,3-Propanedithiol diesters	0.952585 ± 0.010439	−1.7689 ± 0.3628	1.050
1,4-Butanedithiol diesters (low members)	0.892850 ± 0.011746	−1.4730 ± 0.3644	1.120
1,5-Pentanedithiol diesters	1.1293 ± 0.004054	−1.9281 ± 0.1338	0.886

diesters and the 1,5-pentanedithiol diesters are too far removed from the other series to be the same crystalline forms; in fact, too far removed from each other to be the same crystalline forms.

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